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SPECIFICATION

Title of the Invention

Veneer Heat Reflecting Glass

Claims

- (1) A veneer-type heat reflecting glass that comprises a heat reflecting film formed on a glass plate surface and that is suitable for use in automobiles, wherein said veneer heat reflecting glass is characterized by the fact that the heat reflecting film is a laminate comprising a transparent conductor film or transparent conductive oxide film as a first layer (counting in order from the glass plate side), a nitride film as a second layer, a transparent conductor film or transparent conductive oxide film as a third layer, and an oxide thick film as the topmost layer on the third layer with the topmost layer serving as the exposed surface.
- (2) A veneer heat reflecting glass as defined in Claim 1, characterized by the fact that TiN, ZrN, HfN, or a compound nitride of these, is used as the nitride film.
- (3) A veneer heat reflecting glass as defined in Claim 1, characterized by the fact that the refractive index of the oxide thick film that serves as the fourth layer is virtually equal to the refractive index of the glass plate.
- (4) A veneer heat reflecting glass as defined in Claim 1, characterized by the fact that the oxide thick film of the topmost layer is SiO_2 or a transparent oxide having SiO_2 as its predominant component, and has a refractive index between 1.4 and 1.6.
- (5) A veneer heat reflecting glass as defined in Claim 1, characterized by the fact that the thickness of the oxide thick film of the topmost layer is at least $1\ \mu\text{m}$.
- (6) A veneer heat reflecting glass as defined in Claim 1, characterized by the fact that the transparent conductor film or transparent conductive oxide film employs a material having a refractive index of at least 1.8.
- (7) A veneer-type heat reflecting glass that comprises a heat reflecting film formed on a glass plate surface and that is suitable for use in automobiles, wherein said veneer heat reflecting glass is characterized by the fact that the heat reflecting film is a laminate comprising a transparent conductor film or transparent conductive oxide film as a first layer (counting in order from the glass plate side), a nitride film as a second layer, a transparent conductor film or transparent conductive oxide film as a third layer, an additional nitride film as a fourth layer, an additional transparent conductor

film or transparent conductive oxide film as a fifth layer, and an oxide thick film as the topmost layer on the fifth layer, with the topmost layer serving as the exposed surface.

(8) A veneer heat reflecting glass as defined in Claim 7, characterized by the fact that TiN, ZrN, HfN, or a compound nitride of these, is used as the nitride film.

(9) A veneer heat reflecting glass as defined in Claim 7, characterized by the fact that the refractive index of the oxide thick film that serves as the sixth layer is virtually equal to the refractive index of the glass plate.

(10) A veneer heat reflecting glass as defined in Claim 7, characterized by the fact that the oxide thick film of the topmost layer is SiO₂ or a transparent oxide having SiO₂ as its predominant component, and has a refractive index between 1.4 and 1.6.

(11) A veneer heat reflecting glass as defined in Claim 7, characterized by the fact that the thickness of the oxide thick film of the topmost layer is at least 1 μ m.

(12) A veneer heat reflecting glass as defined in Claim 7, characterized by the fact that the transparent conductor film or transparent conductive oxide film employs a material having a refractive index of at least 1.8.

Detailed Description of the Invention

Field of Industrial Utilization

The present invention relates in general to a heat reflecting glass that can be used in automobiles, and in particular relates to a veneer heat reflecting glass that can be used in side windows and rear windows.

Prior Art

The use of heat reflecting glass (solar control glass) or heat absorbent glass in order to block some of the sunlight entering vehicle interiors through window glass, to reduce temperature elevation within the vehicle, to reduce the load on the air conditioner, and to reduce direct light in order to perceptibly lower heat and improve comfort has been studied on a continuing basis. However, in order to ensure sufficient visibility (from a safety standpoint) a standard of at least 70% visible light transmittance has been adopted in Japan and the US; in Europe, the standard is 75%. Films used to coat heat reflecting glass that meets these standards as well as having the required characteristics are limited to transparent oxide film/Ag film (film thickness: 100 Å to 200 Å)/transparent oxide film structures (Japanese Patent Publication 47-6315). Transparent oxides employed in such structures are TiO₂, ZrO₂, HfO₂, SnO₂,

ZnO, In_2O_3 , or mixtures of these. When this structure is employed, visible light transmittance in excess of 80% can be readily achieved.

However, the biggest drawback of heat reflecting glass that employs silver films is that resistance to scuffing and chemical durability are extremely poor. Deterioration begins after being placed in the atmosphere for only a few days. In weatherometer tests, natural exposure tests, constant-temperature constant-humidity tests, and the like, marked deterioration is produced within 1 to 2 days. Thus, heat reflecting glass that employs silver films can only be used as safety glass or double glazing; in the case of automobiles, it is generally used as safety glass. However, the use of such materials as safety glass in automobiles is currently limited to windshields due to cost factors, the durability of the safety glass edges, and other considerations. From this standpoint, there is a need (from a cost standpoint) for a veneer-type product for use as a heat reflecting glass in side windows and rear windows.

The semiconductor materials TiN, ZrN, HfN, and other nitrides are characterized by high hardness and a lustrous gold color. These characteristics are utilized in coating steel and other metal surfaces to produce carbide materials and ornamental articles. The electrical resistance of such material is relatively low, so they show promise as heat reflecting film materials. According to an article published by a Swedish research group (B. Karlsson, C. G. Ribbing, SPIE Vol. 324, "Optical Coatings for Energy Efficiency and Solar Applications" (1982) pp. 52 - 57), sandwiching TiN, ZrN, and HfN thin films between transparent conductors having a high index of refraction affords heat reflecting films that can be substituted for three-layer heat reflecting films employing silver films or other precious metal thin films.

However, in order to obtain nitride films having high hardness and low resistance, it is necessary during film manufacture to raise the substrate temperature to a rather high level (400 to 500°C), which is difficult and inconvenient. This fact represented one reason why it was difficult to use such material in automotive glass, in spite of the fact that nitrides are such useful materials.

Problems Which the Invention Is Intended to Solve

The object of the present invention is to solve the drawback of inferior durability that was inherent to conventional transparent oxide film/Ag film/transparent oxide film system heat reflecting films, and is particularly aimed at improving abrasion resistance. It also offers a way for obtaining such products without the use of any special process, such as heating the substrate, during film manufacture.

Means Used to Solve the Aforementioned Problems

The present invention was developed in order to solve the drawbacks noted above. The first invention offers a veneer-type heat reflecting glass that comprises a heat reflecting film formed on a glass plate surface and that is suitable for use in automobiles, wherein said veneer heat reflecting glass is characterized by the fact that the heat reflecting film is a laminate comprising a transparent conductor film or transparent conductive oxide film as a first layer (counting in order from the glass plate side), a nitride film as a second layer, a transparent conductor film or transparent conductive oxide film as a third layer, and an oxide thick film as the topmost layer on the third layer with the topmost layer serving as the exposed surface; the second invention offers a veneer-type heat reflecting glass that comprises a heat reflecting film formed on a glass plate surface and that is suitable for use in automobiles, wherein said veneer heat reflecting glass is characterized by the fact that the heat reflecting film is a laminate comprising a transparent conductor film or transparent conductive oxide film as a first layer (counting in order from the glass plate side), a nitride film as a second layer, a transparent conductor film or transparent conductive oxide film as a third layer, an additional nitride film as a fourth layer, an additional transparent conductor film or transparent conductive oxide film as a fifth layer, and an oxide thick film as the topmost layer on the fifth layer, with the topmost layer serving as the exposed surface.

Figures 1 and 2 are partial cross sections of the heat reflecting glass which pertains to the present invention. 1 and 11 indicate glass plates selected from colorless transparent or colored transparent soda-lime silicate ordinary sheet glass, float glass, blue, bronze, green, or other colored heat absorbent glass, aluminosilicate glass, lithium aluminosilicate glass, borosilicate glass, and other types of glass. 2 and 12 indicate transparent conductor films or transparent conducting oxide films which serve as first layers. 3 and 13 indicate nitride films which serve as second layers. 4 and 14 indicate transparent conductor films or transparent conducting oxide films which serve as third layers. 15 indicates a nitride film that serves as a fourth layer. 16 indicates a transparent conductor film or transparent conducting oxide film which serves as a fifth layer. 5 and 17 indicate transparent oxide thick films that serve as topmost layers.

The present invention is based on a structure in which a nitride film is substituted for the silver film in the conventional transparent oxide film/Ag film/transparent oxide film system heat reflecting film. TiN, ZrN, HfN, or compound nitrides of these may be used for the nitride film. From the standpoint of optical performance, ZrN or HfN are preferred; TiN is excellent from a cost standpoint. These nitride films are similar to film or precious metals such as silver or gold in terms

of reflection characteristics, but the refractive index n (optical constant) is higher than with precious metals so the film thickness cannot be increased to a great degree. In Japan, standards require automotive glass to have a visible light transmittance of at least 70%, and this necessarily entails restrictions as to maximum film thickness. On the other hand, if the film is too thin, heat reflecting performance will be impaired. For these reasons, the nitride film thickness should be 20 to 250 Å, preferably 40 to 220 Å, and ideally 50 to 200 Å. The transparent conductor film can consist of TiO_2 , ZrO_2 , HfO_2 , Ta_2O_5 , or the like; the transparent conductive oxide film can consist of SnO_2 , In_2O_3 , ZnO , or the like. The film thickness required to achieve the required performance will differ depending on the material selected; due to the 70% visible light transmittance standard (just as with the nitride film), a thickness of 50 to 1000 Å, preferably 100 to 800 Å, and ideally 200 to 600 Å, should be used. It is necessary for the index of refraction to be at least 1.8 in order to achieve a product having this type of high light transmittance. There are no particular restrictions regarding the method of film manufacture. When productivity is a major concern, a sputtering technique may be used; when film quality is of paramount importance, an rf-bias technique, ion plating technique, arc deposition technique, or other such technique produces excellent results.

The oxide thick film that serves as the topmost layer should consist of a material that has an index of refraction virtually equal to that of the glass plate (in the case of the glass plate mentioned above, for example, the index of refraction is 1.4 to 1.6). SiO_2 or a transparent oxide having SiO_2 as its predominant component is the preferred transparent oxide; the material must have a refractive index between 1.4 and 1.6. In order to fully realize the effect of the invention, the thick film must be at least 1 μm thick. A thickness of 1 μm to 10 μm is especially favorable. If the film is thinner than 1 μm , abrasion resistance and scuff resistance will not be improved; a thickness in excess of 10 μm makes the film susceptible to delamination and should therefore be avoided. The method for manufacturing this film can be an ordinary deposition or sputtering technique such as those used for the other layers; however, the thickness of the film makes a dipping technique or similar method more effective. When manufacturing the oxide, the application of substrate bias can improve film quality resulting in more favorable conditions. The thick film consisting of the aforementioned SiO_2 or a transparent oxide having SiO_2 as its predominant component is transparent, has satisfactory physical and chemical durability. Moreover, since the refractive index is virtually equal to that of the glass plate, it has optical properties similar to those of the substrate glass plate. The film thickness of the topmost layer is, for example, 1 μm

to 10 μm , and since this film thickness is significantly longer than the visible light wavelength region, optical characteristics are virtually unaffected by abrasion or soiling; mechanical strength is also excellent, affording a useful heat reflecting film.

The heat reflecting film which pertains to the present invention utilizes interference between the nitride film layer and the transparent conductor film or the transparent conductive oxide film. Thus, suitable selection of film thickness structure affords visible light transmittance of 70% or higher, solar energy transmittance of no more than 60%, and visible light reflectance of no more than 10%. An example of a heat reflecting film structure that affords these optical properties is as follows.

Film structure: SiO_2 film/ TiO_2 film/ ZrN film/ TiO_2 film/glass plate

Film thickness: 2.0 μm /250 \AA /100 \AA /250 \AA /3 mm

The optical characteristics of a heat reflecting glass on which this four-layer heat reflecting film had been formed were measured; the results are presented in Figure 3.

In Figure 3, [A indicates] the transmittance curve and B indicates the reflectance curve.

The following is an example of a six-layer heat reflecting film structure.

SiO_2 film/ TiO_2 film/ ZrN film/ TiO_2 film/ ZrN film/ TiO_2 film/glass plate

2.0 μm /300 \AA /150 \AA /600 \AA /150 \AA /300 \AA /3 mm

Effect of the Invention

In the present invention, the optical characteristics displayed by the products are the result of interference between the nitride film and the transparent conductor film or the transparent conductive oxide film. The product is therefore susceptible to the effects of variations in film thickness, and scratches, soiling, etc., stand out. The provision of an oxide thick film layer as a topmost layer in the present invention serves to ameliorate these effects. For example, when a glass plate is laminated with a 250 \AA TiO_2 film as a first layer, a 100 \AA ZrN film as a second layer, and a 250 \AA TiO_2 film as a third layer, and this product is not provided with any overcoat, the visible light transmittance is 67.5%, the visible light reflectance on the glass side is 12.4%, and the visible light reflectance on the film side is 14.4%. Such a film is susceptible to external mechanical forces, and if it is assumed that 20% of the outermost TiO_2 film has been worn away, the visible light transmittance declines to 67.0%, the visible light reflectance on the glass side to 11.3%, and the visible light reflectance on the film side changes to 14.9%. These values may not appear to change much, but when changes in

reflected color on the glass side (which is the most problematic in terms of film color, and particularly external appearance) are taken into consideration, it must be noted that the color difference reaches 4.32. On the other hand, a film of identical structure furnished with an overcoat (a $2.0\ \mu\text{m}$ SiO_2 film as a topmost layer) has visible light transmittance of 72.2%, a visible light reflectance on the glass side of 8.7%, and a visible light reflectance on the film side of 8.9%. When 20% of the SiO_2 film topmost layer is abraded away, as in the comparative example, the transmittance is 72.2%, the reflectance on the glass side is 8.7%, and the reflectance on the film side is 8.9%. In short, the values are completely unchanged. The change in reflected color on the glass side, expressed in terms of color difference, is only 0.65, approximately 15% that seen in the comparative example. This fact indicates that the provision of an SiO_2 thick film as an overcoat serves to ameliorate changes in reflected color produced by wear.

When characteristics originate in interference, the product is susceptible to the effects of variations in film thickness; it is to be expected that the presence of adhering material will produce variations in color, just as when the film was worn away. The presence of an oxide thick film overcoat can be predicated to ameliorate such changes in this case as well.

In the present invention, the nitride film, the transparent conductor film, and the transparent conductive oxide film are not directly exposed to the outside, so bulk and hardness are not required from these layers. It is sufficient to perform the coating operation as when using ordinary equipment, without raising the substrate temperature to 400 to 500°C. When the difficulty entailed in heating a relatively large surface area to a uniform temperature is considered, it is clear that this fact is extremely significant in terms of reduced difficulty and cost. Moreover, since the color change (expressed in terms of the color difference) when 20% of the SiO_2 film is worn away, as in the example described above, is a mere 0.65, significant changes in film thickness produced by wear are permissible. Since the SiO_2 film thickness is, for example, $2\ \mu\text{m}$, [such changes] can be on the order of several thousand Å. This indicates that bulk and hardness are not required from the topmost oxide thick film layer either (just as with the other layers), and its manufacture can be a relatively simple affair.

Practical Examples

Practical Example 1

Metallic titanium and SiO_2 were placed as targets in a high-frequency magnetron sputtering device. A soda-lime glass plate (3 mm thick) whose surface had

been cleaned by polishing or other means was placed in a vacuum chamber which was then evacuated to 1.0×10^{-5} torr using an oil diffusion pump. A mixed gas ($\text{Ar}:\text{O}_2 = 4:6$) was first introduced into the vacuum chamber to bring the pressure to 3.0×10^{-3} torr. Power (5.1 Kw/cm^2) was applied to the titanium target and sputtering was performed for 11 minutes and 20 seconds until the TiO_2 film grew to 500 \AA . Next the atmosphere of the vacuum chamber was completely exchanged with a mixed gas ($\text{Ar}:\text{N}_2 = 82.5:17.5$), adjusting the pressure to 1.2×10^{-3} torr. Power (4.6 Kw/cm^2) was applied to the titanium target and sputtering was performed for 15 seconds until the TiN film grew to 100 \AA . Next, the atmosphere was returned to an $\text{Ar}:\text{O}_2 = 4:6$ mixed gas, and a 500 \AA TiO_2 film was grown. Finally, the atmosphere of the vacuum chamber was replaced with 100% argon to bring the sputtering pressure to 2.5×10^{-3} torr, power (3.1 Kw/cm^2) was applied to the SiO_2 film target and sputtering was performed for 60 minutes until the SiO_2 film grew to $1.6 \text{ }\mu\text{m}$. The optical characteristics of the four-layer coated heat reflecting glass obtained in this way were measured. Visible light transmittance was 73.0% and sunlight transmittance was 59.3%. This sample was subjected to a sand eraser test under a load of 500 g at a speed of 50 mm/min. Virtually no damage was noted after 8 cycles.

Practical Example 2

Metallic titanium and SiO_2 were placed as targets in a high-frequency magnetron sputtering device. An arc deposition device having metallic zirconium as an arc target was attached. A soda-lime glass plate (3 mm thick) whose surface had been cleaned by polishing or other means was placed in a vacuum chamber which was then evacuated to 1.0×10^{-5} torr using an oil diffusion pump. A mixed gas ($\text{Ar}:\text{O}_2 = 4:6$) was first introduced into the vacuum chamber to bring the pressure to 3.0×10^{-3} torr. Power (5.1 Kw/cm^2) was applied to the titanium target and sputtering was performed for 6 minutes and 50 seconds until the TiO_2 film grew to 300 \AA . Next the atmosphere within the vacuum chamber was completely exchanged with 100% N_2 , adjusting the pressure to 5.0×10^{-3} torr. A 60 A arc current was applied to the zirconium target until the ZrN film grew to 200 \AA . Next, the atmosphere was returned to an $\text{Ar}:\text{O}_2 = 4:6$ mixed gas, and a 300 \AA TiO_2 film was grown. Finally, the atmosphere of the vacuum chamber was replaced with 100% argon to bring the sputtering pressure to 2.5×10^{-3} torr, power (3.1 Kw/cm^2) was applied to the SiO_2 film target and sputtering was performed for 75 minutes until the SiO_2 film grew to $2.0 \text{ }\mu\text{m}$. The optical characteristics of the four-layer coated heat reflecting glass obtained in this way were measured. Visible light transmittance was 70.2% and

sunlight transmittance was 49.6%. This sample was subjected to a sand eraser test under a load of 500 g at a speed of 50 mm/min. Virtually no damage was noted after 8 cycles.

Practical Example 3

Metallic titanium and SiO_2 were placed as targets in a high-frequency magnetron sputtering device. An arc deposition device having metallic zirconium as an arc target was attached. A soda-lime glass plate (3 mm thick) whose surface had been cleaned by polishing or other means was placed in a vacuum chamber which was then evacuated to 1.0×10^{-5} torr using an oil diffusion pump. A mixed gas ($\text{Ar}:\text{O}_2 = 4:6$) was first introduced into the vacuum chamber to bring the pressure to 3.0×10^{-3} torr. Power (5.1 Kw/cm^2) was applied to the titanium target and sputtering was performed for 6 minutes and 50 seconds until the TiO_2 film grew to 300 Å. Next, the atmosphere within the vacuum chamber was completely exchanged with 100% N_2 , adjusting the pressure to 5.0×10^{-3} torr. A 60 A arc current was applied to the zirconium target until the ZrN film grew to 150 Å. Next, the atmosphere was returned to an $\text{Ar}:\text{O}_2 = 4:6$ mixed gas, and a 600 Å TiO_2 film was grown. Next the pressure was adjusted to 5.0×10^{-3} torr, a 60 A arc current was applied to the zirconium target, and a 150 Å ZrN film was grown. Next, the atmosphere was returned to an $\text{Ar}:\text{O}_2 = 4:6$ mixed gas, and a 300 Å TiO_2 film was grown. Finally, the atmosphere of the vacuum chamber was replaced with 100% argon to bring the sputtering pressure to 2.5×10^{-3} torr, power (3.1 Kw/cm^2) was applied to the SiO_2 film target and sputtering was performed for 80 minutes until the SiO_2 film grew to 2.2 μm . The optical characteristics of the four-layer [sic] coated heat reflecting glass obtained in this way were measured. Visible light transmittance was 70.2% and sunlight transmittance was 43.2%. This sample was subjected to a sand eraser test under a load of 500 g at a speed of 50 mm/min. Virtually no damage was noted after 8 cycles.

Comparative Example

Following the method of Practical Example 1, a 600 Å TiO_2 film was grown, followed by a 200 Å TiN film and a 600 Å TiO_2 film. Formation of the final SiO_2 film was not performed. The optical characteristics three-layer coated heat reflecting glass obtained in this way were measured. Visible light transmittance was 71.8% and sunlight transmittance was 51.9%, but when the sample was subjected to a sand eraser test under a load of 500 g at a speed of 50 mm/min, noticeable damage occurred after two cycles.

Merits of the Invention

The present invention involves providing a film conferred with heat reflecting performance by lamination of a transparent conductor film or a transparent conductive oxide film and a nitride film with an overcoating with an oxide thick film as the topmost layer, resulting in a lessening of interference color changes due to film abrasion of the adhesion of foreign material; the product thus afford a heat reflecting film that is durable enough to be practical, without requiring an special treatment such as raising the substrate temperature.

4. Brief Description of the Figures

Figures 1 and 2 are partial cross sections of the heat reflecting glass which pertains to the present invention. Figure 3 illustrates the optical characteristics of a heat reflecting glass pertaining to a specific practical example of the present invention.

1, 11--glass plate

2, 12, 4, 14, 16--transparent conductor film or transparent conductive oxide film

3, 13, 15--nitride film

5, 17--oxide thick film

Figure 1

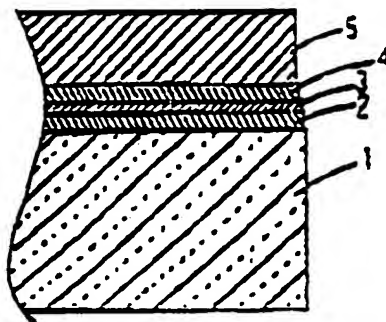


Figure 2

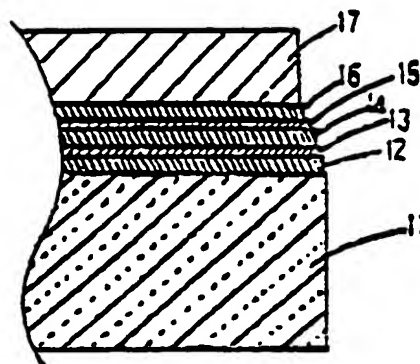


Figure 3

